COLLOIDAL STRUCTURE OF VACUUM RESIDUE IN SOLVENTS

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I. Introduction

    Petroleum asphaltenes form colloidal particles in organic solvents through self-association, when the concentration exceeds a threshold value [1-5]. The self-association process is very similar to the micellization process of surfactant systems [6]. Since the structure, size and the polydispersity of the asphalteme colloids are important parameters for developing technology to upgrade vacuum residue, it is necessary to establish an analytical technique capable of accurately evaluating these parameters. Small angle neutron scattering (SANS) has been sucessfully applied to the structural characterization of micellar solutions [7]. We employed this technique in this study to investigate asphaltenes. Unfortunately, the polydispersity and the intercolloidal interactions often complicate the data analysis, and lead to ambiguous results, due to local convergence in the data fitting process. Recently, Sheu [8] developed a self-consistent scheme, by which the particle size distribution can be unambiguously determined from a scattering measurement. This technique however, can only be applied for dilute systems, since the intercolloidal interactions were not taken into account.

    In this study, we followed up on the polydispersity work of Sheu, with the interparticle interaction taken into account. We also studied the effect of solvent permittivity on particle structure, polydispersity and interparticle interactions.

II. Experimental

A. Sample Preparation

    Asphaltene fractions were extracted from Ratawi (Neutral Zone) vacuum residue, by mixing with heptane (1 gram of vacuum residue with 40 cm^3 of heptane) at room temperature. After stirring overnight, the solution was filtered with Whatman number 5 filter paper. The insoluble portion was dried under a stream of nitrogen, until constant weight was maintained for a 48 hour period. This insoluble fraction was taken as the aspaltene fraction.

    To prepare the samples for the SANS measurement, asphaltenes were dissolved in deuterated toluene/pyridine mixtures of various volume ratios, and aged for several days to ensure thermodynamic equilibrium [9]. Toluene has a permittivity of 2.4, while pyridine is 12, the samples were perpared to exhibit the following permittivities: 2.4, 3.84, 5.28, 6.72, and 9.12.

B. SANS Measurement

    The SANS experiment was conducted on the small angle diffractometer (SAD) at Argonne National Laboratory. The neutrons were generated by a neutron generator via Pu-Be reaction. The generated neutron wave lengths were sorted by the time-of-flight method, in order to fully utilize the generated neutrons. The scattering vector Q $(Q = (4\pi/\lambda) \sin \theta)$ was conputed by built-in software using neutron

energy. Therefore, the sample-to-detector distance was fixed. The temperature was maintained at 22 °C.

III. Scattering Theory

The intensity as a function of the scattering vector, $I(Q)$, represents the differential cross section per unit volume of the sample. $I(Q)$ is a function of concentration, particle-solvent contrast, particle structure, and interparticle interactions [10],

$$I(Q) = C (\Delta\rho)^2 [<V_p^2> / <V_p>] <P(Q)> <S(Q)> \qquad (1)$$

where C is concentration, $\Delta\rho$ is the particle-solvent contrast, $<V_p^2>$ is the second moment of particle volume, and $<V_p>$ is the average particle volume. $<P(Q)>$ is the average form factor, governed by particle structure, and $<S(Q)>$ is the average structure factor, governed by interparticle interactions. The evaluation of $<V_p^2>$, $\Delta\rho$, $<V_p>$ and $<P(Q)>$ are described in references 1 and 9.

To calculate $<S(Q)>$, we approximated $<S(Q)>$ by $S(Q)$ (the monodispersed particle structure factor) using $<R>$ (the average particle radius) as the particle size. This approximation is generally plausible [10].

We computed $S(Q)$ by solving the Ornstein-Zernike equation using a mean spherical approximation ansatz. A one-tailed Yukawa potential was used as a direct correlation function [10]. A fortran program was developed to compute $S(Q)$, along with $<P(Q)>$. This program enabled us to unambiguously determine both particle structure and interparticle interactions.

IV. Results

Fig. 1 displays the scattering intensity $I(Q)$ (open circles) and the fitted curve (solid line). The fitting is reasonable for Q up to ~ 0.2 Å^{-1}. Fig. 2 shows the average radius $<R>$ and the Yukawa parameter, K, as a function of solvent permittivity. K represents the "diffusiveness" of the Yukawa potential,

$$V(r) = A \cdot Exp (-Kr)/Kr, \quad r > <R>$$

where A is an amplitude factor representing the contact potential at $r = <R>$. As one can see from Fig. 2, the average radius does not depend on solvent permittivity, but the diffusiveness of the interparticle interaction increases (K decreases). This indicates that the range of interaction increases. Obviously, this is due to "effective" charges on the asphaltene colloids, which result in long range interactions when solvent permittivity increases. Fig. 3 shows the polydispersiy as a function of solvent permittivity. It was found to increase substantially as a function of solvent permittivity. From Gibbs' equilibrium condition this result clearly indicates that for permittivities up to ~9.0, the solvent quality decreases as a function of permittivity [10].

V. Disscussion

In aqueous solutions, the K in Yukawa potential is equal to kR, where k is the Debye screening length. In our case, the solvents were oil-like, which may change the meaning of K. Therefore, K can only be visualized as a parameter characterizing the "diffusiveness" of the the potential.

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As for the polydispersity, we argue based on the first principle given by Gibbs, about thermal equilibrium. Based on Gibbs' equilibrium condition, the polydispersity should increase when the solvent quality becomes poorer, in order to optimize the free energy through eutropic energy [10.11]. This finding leads us to conclude that the asphlatene colloids behave similarly to surfactant solutions, and by tuning the solvent permittivity, dispersion of asphaltene colloids may be possible. This conclusion may shed light on the upgrading of vacuum residue.

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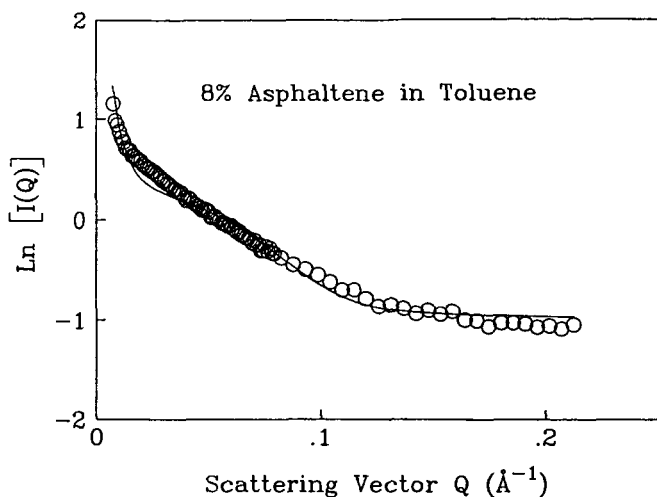
Fig. 1. Fitting of a 8% asphaltene solution. The SANS data (circles), and the theoretical curve (solid line) agree reasonably well, indicating that a one-tailed Yukawa potential is an appropriate representation of the interactions between asphaltene colloids .
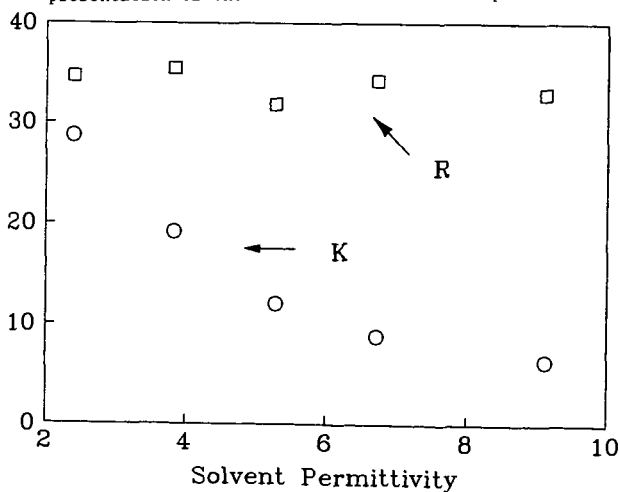

Fig. 2. Average particle radius and potential diffusiveness as a function of the solvent permittivity. The diffusiveness increases (K decreases) as a function of the solvent permittivity, while the average radius remains nearly unchanged.
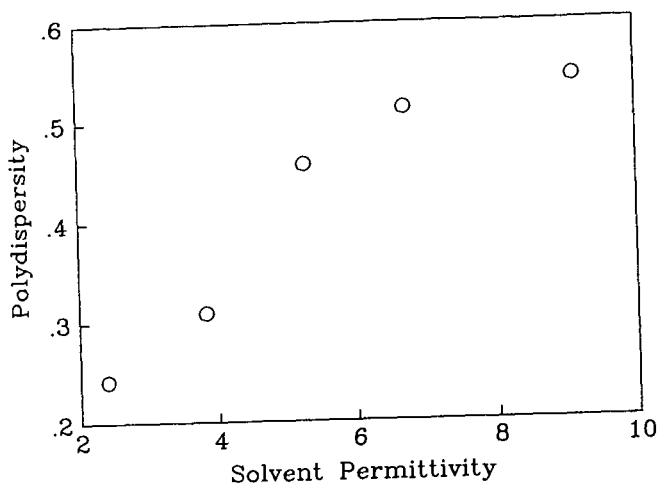
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Fig. 3. Polydispersity, as a function of the solvent permittivity, for an 8% asphaltene concentration.